

FEDERAL REPUBLIC OF GERMANY

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Union Priority : 10-16-1986 CS 7492-86Applicant: : Ceskoslovenska Akademie ved,
Prague, CSLegal Representative : Beetz sen. & Partners,
Patent Attorneys
8000 MunichInventors : Hudecek, Slavko, Dr. et al
Prague, CS

Title: COPOLYMERS OF ACRYLIC AND/OR METHACRYLIC ACID
WITH OLIGO-URETHANE-MACROMONOMERS, THEIR PREPARATION
AND THEIR APPLICATION

The invention relates to copolymers of acrylic or methacrylic acid or their alkali metal salts, with macromonomers based on oligo-urethanes having the general formula:

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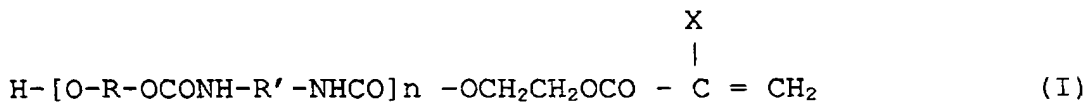
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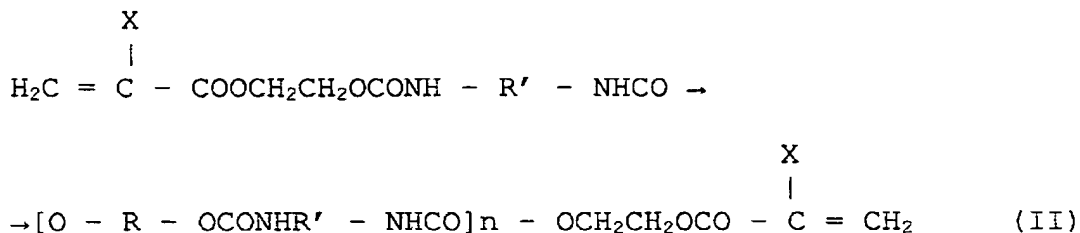
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Title: COPOLYMERS OF ACRYLIC AND/OR METHACRYLIC ACID
WITH OLIGO-URETHANE-MACROMONOMERS, THEIR PREPARATION
AND THEIR APPLICATION

The invention relates to copolymers of acrylic or methacrylic acid or their alkali metal salts, with macromonomers based on oligo-urethanes having the general formula:



or the general formula II:



and/or suitable mixtures thereof wherein

R is the radical of a low-molecular aliphatic diol with
2 to 4 C-atoms;

R' is the radical of an aliphatic, aromatic or
aliphatic-aromatic diisocyanate;

X is H or CH₃; and

n is an integer from 2 to 40,

whereby the composition preferably amounts to 0.5 to 10
parts by mass of the macromonomer per 100 parts by mass of
acrylic and/or methacrylic acid or their alkali metal
salts.

The copolymers as defined by the invention can be
produced according to the usual methods of copolymerization
and are capable of absorbing large amounts of water or body
fluids. They are therefore suitable as materials for

removing water particularly for medical purposes. They can be used also in the form of swollen gels.

Description

The invention relates to copolymers of acrylic acid and/or methacrylic acid or their alkali metal salts with macromonomers based on oligo-urethanes, and to a method for their preparation, as well as to their application as or in sorbent agents. Said copolymers are capable, for example, of absorbing large amounts of water and are therefore suitable for removing water, or for application in the form of gels in the swollen state.

As materials capable of absorbing water, substances of natural origin such as non-woven cellulose or cotton fibers as well as quasi sponge-like natural or synthetic materials have been used until now primarily for medical and medicinal purposes. Such substances and materials are used for producing all kinds of different, in particular medical articles such as diapers, powder etc. However, such materials and substances do not by far possess the capability of absorbing adequate quantities of water or body fluids.

Novel materials that are based on water-soluble polymers or copolymers have been proposed for said reason in the last few years for such purposes. Their solubility is practically eliminated by cross-linking with the help of cross-linking agents, i.e. compounds containing two or more reactive functional groups such as, for example unsaturated compounds; compounds that contain epoxy groups, etc.

Another way of reducing the solubility is to partly substitute lipophilic groups for the hydrophilic groups.

Such materials were produced, for example by copolymerization of acrylic acid with ethylene glycol dimethacrylate, or of methacrylic acid with divinyl benzene (US 4,379,868 A); or of acrylamide with N,N'-alkylidene(bis-acrylamides); or of ethylene glycol diacrylate with divinyl benzene (JP 68 23 468 B) by cross-linking of N-hydroxy-acrylamide under exposure to light at low temperatures (JP 69 31 823 B); by copolymerizing polyol-methacrylates with unsaturated acids or monomers containing basic groups, in the presence of ethylene glycol diacrylate, methylene-bis(acrylamide), or divinyl benzene (JP 7325 749 B), as well as, for example by copolymerizing unsaturated carbonic acids or sulphoacids with polyalkylene

diacrylates or polyethylene glycol diglycidyl ethers (GB 20 81 725 B).

Furthermore, known is the production of copolymers of ethylene vinyl ethers, vinyl acetate and esters of the acrylic acid, e.g. methylmethacrylate, with divinyl benzene, which are subjected to saponification in the last stage (JP 7 81 04 691 B).

Polysaccharides (starches, cellulose, etc.) grafted with acrylo-nitrile, following saponification, also supply products with rather high water absorption power (US 3,661,815 A and US 3,669,103 A). Also polysaccharides produced by direct polymerization, which are grafted with acrylic or methacrylic acid, exhibit similar properties (JP 82 38 809 B), as well as materials that are obtained by modifying polyvinyl alcohol with the sodium salt of acrylic or methacrylic acid (DE 29 35 712 A1).

However, the materials specified above pose a number of problems in their practical application, of which the main problems are the inadequate absorption of water and body fluids, and the fact that some of the production processes are very complicated. In addition, there is the problem

that with some of these conventional materials, when used in the long term in the swollen state, i.e. in the form of a gel, a structural degradation occurs as a result of their low stability.

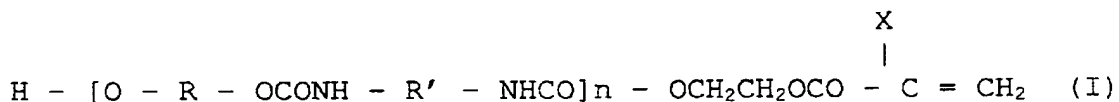
The invention is based on the task of proposing novel types of copolymers based on acrylic or methacrylic acid, and their preparation. Said novel copolymers are characterized by their high sorption and in particular absorptive power for water and similar liquids, simple production, and high chemical stability also in the form of swollen gels, and are therefore applicable in a favorable manner as sorption and absorption agents.

The problem is solved according to the independent claim. Advantageous embodiments of the invention are the object of the dependent claims.

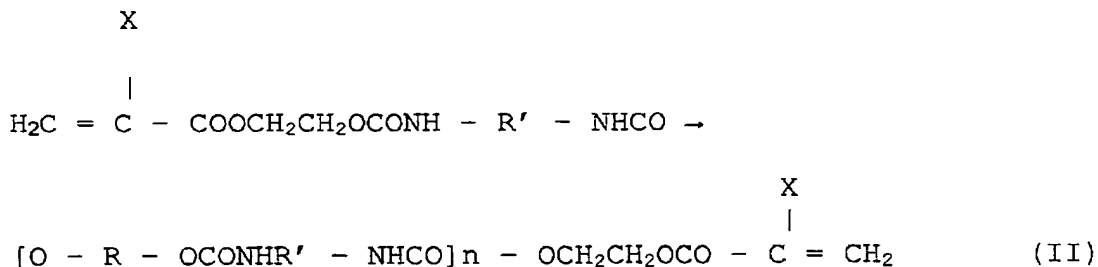
The copolymers as defined by the invention are copolymers of

- (A) acrylic and/or methacrylic acid or their alkali metal salts with

(B) macromonomers based on oligo-urethanes having on one or both ends of the chain unsaturated acrylate or methacrylate groups, of the general formula I:



and/or II:



wherein

R is the radical of a low-molecular aliphatic diol with 2 to 4 C-atoms;

R' is the radical of an aliphatic, aromatic or aliphatic-aromatic diisocyanate;

X is H or CH₃; and

n is an integer from 2 to 40; or the corresponding macromonomer mixtures.

The copolymers preferably have 0.5 to 40 parts by mass of units originating from the macromonomers having the formula I and/or II, per 100 parts by mass of units

originating from the acrylic and/or methacrylic acid or their alkali metal salts.

As suitable diisocyanates it is possible to use aliphatic diisocyanates such as hexamethylene diisocyanate, aromatic diisocyanates such as p-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, or their mixtures; m-xylylene diisocyanate or 1,5-naphthalene diisocyanate, as well as alkylaromatic diisocyanates such as 4,4'-methylene-bis(phenylisocyanate) and 4,4'-ethylene-bis(phenylisocyanate). The bifunctional oligo-urethane is formed by polyaddition reaction in the presence of low-molecular diols such as ethylene glycol, propylene glycol, 1,4-butane-diol, and 3-oxa-1,5-pentane-diol.

The oligo-urethane with one or two terminal vinyl groups is produced either in two stages by letting the diisocyanate first react with the hydroxyalkylacrylate or hydroxyalkylmethacrylate and, upon completion of the reaction, carrying out the polyaddition with the respective diol, or also in one stage, in which case both compounds containing hydroxyl groups, i.e. the monohydroxy- and the dihydroxy compound are simultaneously reacted with the diisocyanate. In both cases, the chain growth is stopped by

the hydroxylalkyl ester, which consequently acts as the agent breaking off the chain.

The preparation of said macromonomers based on oligourethanes with one or two terminal unsaturated double bonds of the acrylate or methacrylate type is described in CS-patent 2 23 409 (1983), as well as in US 4,584,354 A.

The capability of absorbing water and body fluid, and as an indirect consequence also the mechanical properties of corresponding gels in the swelled state, are dependent upon the quantitative ratio of the two components of the copolymers. A ratio of 0.5 to 10 parts by mass macromonomers per 100 parts by mass acrylic and/or methacrylic acid or their alkali metal salts, i.e. the sodium or potassium salts, is selected depending on the required properties.

The actual copolymerization reaction can be carried out by generally known methods comprising the use of initiators or initiator systems leading to radical copolymerization, such as, for example dibenzoyl peroxide, cumolhydroperoxide, cyclohexanol peroxide, diacetyl peroxide, diisopropylperoxo-carbonate, di-t-butyl peroxide,

azo-bis(isobutyro-nitrile), or potassium or ammonium peroxodisulfate, or also by using combinations of said initiators with compounds with reducing properties such as, for example, ascorbic acid, sodium thiosulfate, or oxyacetone, and metal ions such as Fe^{2+} -ions or Cu^{+} -ions. The reaction can be carried out either without solvent in the form of a block copolymerization, or in the presence of solvents, preferably of water, alcohols and/or ketones, and, if need be, aprotic solvents such as dimethyl formamide or N-methylpyridine, if necessary in the form of their mixtures with water.

It has already been demonstrated in the past that the copolymerization of the low-molecular monomers 2-hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, or N-vinyl-pyrrolidone, which are commercially available, with macromonomers of the oligo-urethane type leads to relatively high mechanical strength of the final products in the swelled state (US 4,656,236 A, CS patent 2 50 939).

Now, it has been found within the framework of the invention that this phenomenon occurs also in the copolymerization of acrylic and/or methacrylic acid or

their alkali metal salts because the corresponding copolymers, when swelled in distilled water to 10,000% to 35,000% of the original mass, i.e. with a solids content of 0.286 to 1%, still exhibit good mechanical properties.

The swelling was determined in conjunction with said high-swelling materials in that 0.5 g of the crushed or ground copolymer was charged in a 250-ml measuring flask, which was then filled up with distilled water. After 24 hours of standing, the swelling was determined by dividing the value obtained for the gel volume by 0.5, or by multiplying it with 2. Multiplication of the result with 100 supplies the final result in %.

The above and the following examples show that the preparation of the copolymers as defined by the invention is very simple and can be carried out by the usual methods.

Example 1

Preparation of an oligo-urethane (macromonomer) with a molecular mass $\bar{M}_n = 2300$:

A 1000-ml glass reactor equipped with a double jacket connected to a thermostat, reflux cooler with calcium chloride closure, feed tube for dry nitrogen and

thermometer was charged with 82.4 ml hexamethylene diisocyanate (NCO-content 98.3% of theory), 9.15 ml 2-hydroxyethyl methacrylate, and 1.5 g tetrabutyl tin. The mixture was stirred for 2 hours under an inert atmosphere at 50°C. The mixture was subsequently mixed with 300 ml dimethy-formamide; following homogenization, 53 g 2,2'-dioxidiethanol (diethylene glycol) dissolved in 300 ml dimethyl-formamide, as well as 4.5 ml tetrabutyl tin was added. The reaction was then continued for another 6 hours. Thereafter, the product was precipitated by pouring the reaction mixture under stirring into 8 liters of distilled water and leaving it standing overnight at room temperature. The precipitate was removed by suction, washed, and then dried under vacuum to mass constancy.

Obtained was 108 g of a dry, powdery product that had a mean molecular mass M_n of 2300, which was determined by ^1H -NMR spectrometry based on the content of terminal double bonds (11 mol-%).

Example 2

A 100-ml Erlenmeyer flask was charged with 50 g freshly distilled acrylic acid, 2.5 g of the macromonomer prepared in example 1 based on oligo-urethanes with a molecular mass

M_n of 2300 and a content of 11 mol-% double bonds, and 50 g azo-bis-isobutyro-nitrile. Following thorough mixing with a magnetic agitator, the mixture was filled into 8 10 ml-ampoules that had been flushed before with nitrogen. After sealing the ampoules by fusion, the copolymerization reaction was carried out in two stages as follows: first 20 hours at room temperature, whereby the main part of the reaction process took place in the course of about 3 h, and subsequently 16 h at 40°. After removing the material from the ampoules, the product was ground on a turnstile-type grinder and 12,5 liters 0,05M sodium hydroxide solution was poured over the material.

After 24 hours, the liquid above the swelled gel was decanted and washed twice, using 1 liter of distilled water each time. After the last decanting of the water (pH 6.5), 500 ml ethanol was added which resulted in substantial deswelling of the gel, while preserving its grain structure. The gel was then filtrated off and dried in a vacuum dryer at 40°. One gram (1 g) of the powdery product obtained showed in distilled water a swelling volume of 210 ml.

Example 3

Preparation of an oligo-urethane (macromonomer) based on diphenylmethane diisocyanate with a molecular mass \bar{M}_n of 2800:

60 g 4,4'-methylene-bis(phenylisocyanate) (MDI), 440 g dimethyl-formamide and 4.68 g 2-hydroxyethyl-methacrylate (HEMA) was loaded in weighed portions in a glass reactor of the same type as the one used in example 1. Said mixture was heated to 50°C under nitrogen atmosphere and maintained at said temperature for 2 hours. Thereafter, a mixture of 15.26 g diethylene glycol (DEG) and 8.47 g 1,4-butane-diol (BD) was added. The reaction was then continued for another 4 hours. The applied molar ratio of the starting components was as follows: MDI:HEMA:PEG:PD (sic) = 1.0:0.15:0.6:0.4.

Upon completion of the reaction, the reaction mixture was cooled to room temperature and the product was precipitated under intensive stirring in 10 liters of distilled water, and then processed as in example 1. After drying, 86 g (98% of theory) of the powdery macromonomer with an average molecular mass \bar{M}_n of 2870 was obtained, which was determined as in example 1.

Example 4

A glass flask equipped with an agitator, a feed tube for nitrogen and a thermometer was charged with 10 g freshly distilled acrylic acid, 50 ml 3M aqueous sodium hydroxide solution, and 0.02 g of the macromonomer with $\overline{M}_n = 2870$ prepared in example 3. The reaction mixture was subsequently flushed with nitrogen and mixed with 0.25 ml ammonium peroxy-disulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the form of a 1% solution, as well as with 0.25 ml of a 6% aqueous solution of triethanolamine. Under stirring, the temperature was then raised to 40°C and maintained at that level for 6 hours. The reaction product was washed with 50% aqueous ethanol and dried for 24 hours at reduced pressure at a temperature of 50°. The absorption of distilled water came to 31,000%.

Example 5

Model tampons for medicinal purposes:

The copolymerisute of example 2 was filled in the granular form in an amount of 0.1 g (with 0.001 g accuracy) in small pouches of unglued cellulose paper, of the type used for packaging tea in portions.

Subsequently, the small pouches were sealed with strips of aluminum foil, weighed, and immersed in

- (1) distilled water
- (2) physiological solution with 0.9 mass-% NaCl, and
- (3) blood plasma.

An empty pouch sealed with aluminum foil was used in the same way as the control specimen.

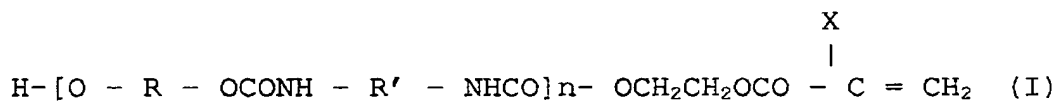
After 24 hours, the small pouches were removed from the liquids and weighed, whereupon the sorption capacity was determined.

Results:	(mass-%)
(1) Distilled water	: 10 700
(2) Physiological solution	: 860
(3) Blood plasma	: 1070

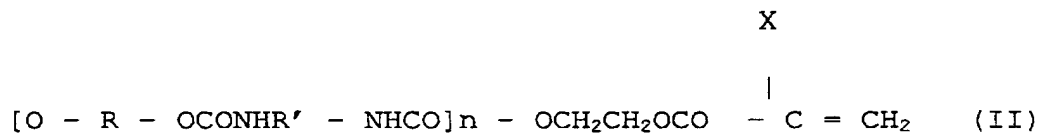
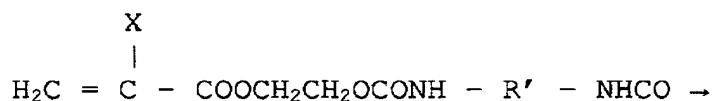
Claims

1. Copolymers of

- (A) acrylic and/or methacrylic acid or their alkali metal salts, with
- (B) macromonomers based on oligo-urethanes having unsaturated acrylate or methacrylate groups on one or both chain ends, said groups having the following general formula I:



or II:



where

R is the radical of a low-molecular aliphatic diol

with 2 to 4 C-atoms;

R' is the radical of an aliphatic, aromatic or aliphatic-aromatic diisocyanate;

X is H or CH₃, and

n is an integer from 2 to 40,

or the corresponding macromonomer mixtures.

2. The copolymers according to claim 1, characterized by 0.5 to 40 parts by mass of units originating from macromonomers of the formulas I and/or II per 100 parts by mass of units originating from acrylic and/or methacrylic acid or their alkali metal salts.

3. The copolymers according to claim 1 or 2, characterized in that the carboxyl groups are partly or wholly present in the free form.

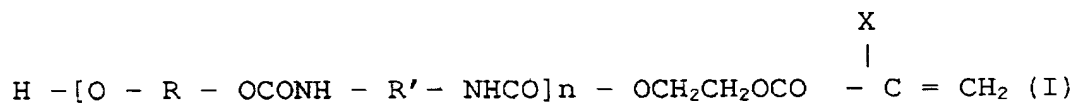
4. The copolymers according to claim 1 or 2, characterized in that the carboxyl groups are partly or wholly present in the form of the corresponding alkali metal salts.

5. The copolymers according to any one of claims 1 to 4, characterized in that they are present in the form of swelled gels, flat materials, fabrics, granulates or powders.

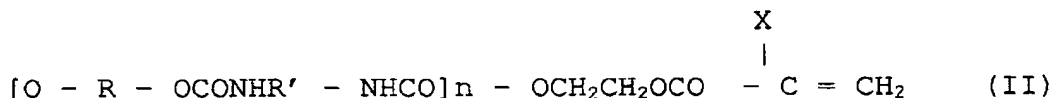
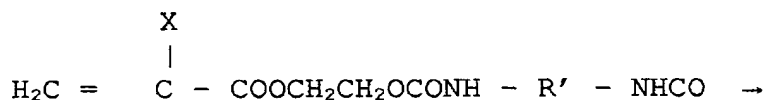
6. A method of producing copolymers according to any one of claims 1 to 5, characterized by the per-se known copolymerization of

(A) acrylic and/or methacrylic acid or their alkali metal salts with

(B) macromonomers having the general formula I



and/or II



where

R is the radical of a low-molecular aliphatic diol with 2 to 4 C-atoms;

R' is the radical of an aliphatic, aromatic or aliphatic-aromatic diisocyanate;

X is H or CH₃; and

n is an integer from 2 to 40.

7. The method according to claim 6, characterized by the use of the co-monomers (A) and (B) in such quantitative ratios that the resulting copolymers contain 0.5 to 40 parts by mass of units originating from the macromonomers

of the formulas I and/or II per 100 parts by mass of units originating from acrylic and/or methacrylic acid or their alkali metal salts.

8. The method according to claim 6 or 7, characterized in that the copolymerization is carried out solvent-free as a block copolymerization, or in the presence of one or more solvents.

9. The use of the copolymers according to any one of claims 1 to 5 as agents for absorbing water, tissue fluids, and body and wound secretions.

10. Sorption agents characterized by the content of one or more copolymers according to any one of claims 1 to 5.